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Enhance Silicon-Nitride Formation Through Ammonolysis of Silanes with Pseudo-halide Substituents

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Supporting Information

CONTENTS

Ammonolysis reaction using SiH_3X model (X = F, Cl, Br and I)

We conducted barrier calculations for the ammonolysis reaction of SiH_3X, where X represents F, Cl, Br, and I at M06-2X/6-311G(d,p) level. The calculated activation barriers and reaction energies are summarized in the below Table. Notably, there is a descending trend in activation barriers as we move down the halogen group, with X = F > Cl > Br > I. The iodine substituent exhibits the slightly lowest barrier at 16.9 kcal/mol compared to bromine at 17.6 kcal/mol.

$SiH_3X + NH_3 \rightarrow SiH_3NH_2 + HX$

X	**ΔG**	**$\Delta G^{\neq}$**
F	17.2	33.9
Cl	8.2	19.8
Br	8.9	17.6
I	7.2	16.9

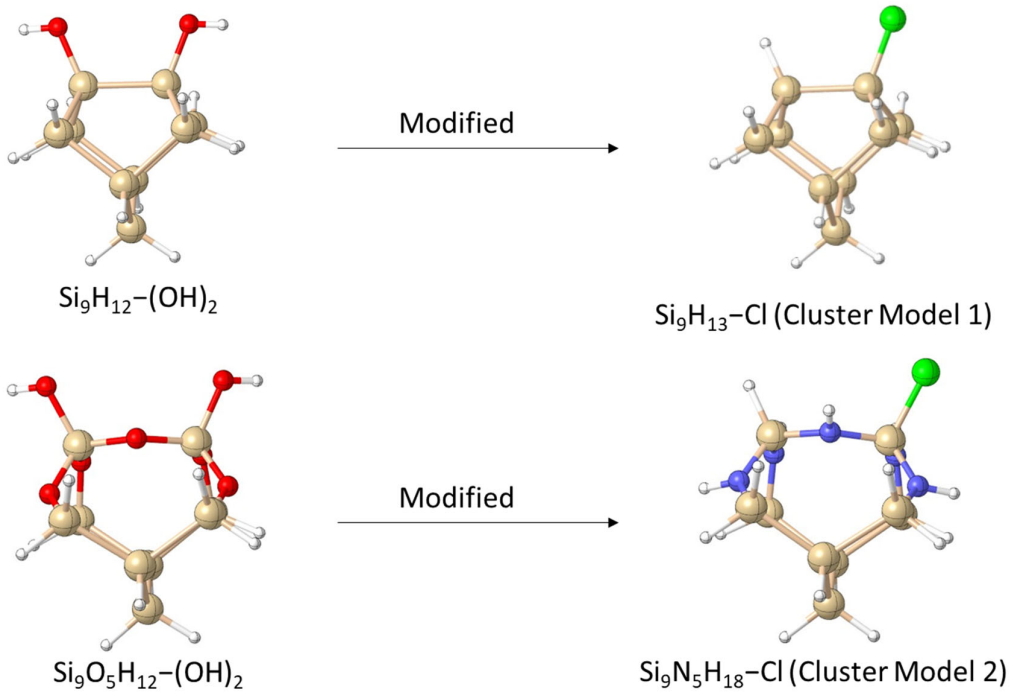
values are in kcal/mol

he primary goal of this paper is to evaluate the ammonolysis barriers of halides and pseudo-halides accurately using a more extensive basis set, namely 6-311++G(3df,2p). Due to the unavailability of the corresponding basis set for the iodine element, the iodine substituent (X = I) has been excluded from this study

Construction of the cluster models

To investigate surface reactions on the SiO_2 bulk surface, Fang, G., et al.[1] have proposed the adoption of two cluster models: the double-hydroxyl $Si_9O_5H_{12}–(OH)_2$ cluster model, and the $Si_9H_{12}–(OH)_2$ cluster model. These models are derived from the fully oxidized Si(100) surface and resemble the hydroxylated α-SiO2 $(10\bar{1}0)$ surface.

In both cluster models, one of the hydroxyl group is replaced with Cl atom and other hydroxyl group is replaced with just hydrogen atom. Remaining 5 oxygen atoms in $Si_9O_5H_{12}–(OH)_2$ cluster model are replaced with NH groups. Schematic representation of modified cluster models for the current study is as shown below. We called Si_9H_{13}-Cl as cluster Cluster Model1 and $Si_9N_5H_{18}$-Cl as cluster 2 in this paper. color code is green for Cl, blue for N, red for O, grey for Si, white = H.



References

1. Fang, G., et al., *Surface Pseudorotation in Lewis-Base-Catalyzed Atomic Layer Deposition of SiO2: Static Transition State Search and Born–Oppenheimer Molecular Dynamics Simulation.* The Journal of Physical Chemistry C, 2012. **116**(50): p. 26436-26448.

Table S1: Summery of reaction energies and barriers (in kcal/mol) of ammonolysis reaction between SiH_3X and NH_3 for all 33 substituents at M062X/6-311++G(3df,2p).

X	$SiH_3X + NH_3 \rightarrow SiH_3NH_2 + HX$	
	Reaction Energy	**Reaction Barrier**
H	-7.5	51.9
F	19.3	37.7
Cl	10.6	23.6
Br	10.1	20.6
CH_3	-13.5	58.6
CF_3	-18.7	44.5
CF_2CN	-16.7	39.1
CN	-1.5	35.2
$P(CH_3)_2$	-11.5	46.8
PF_2	-14.9	49.9
PH_2	-8.8	46.0
$P(CF_3)_2$	-8.5	31.8
NH_2	-0.2	42.5
NCO	10.1	35.0
N_3	5.5	33.1
NCS	11.3	31.0
NCSe	13.7	28.6
OH	9.0	40.9
OCH_3	9.8	39.2
OF	6.9	30.2
OCF_3	9.6	27.5
OCN	-13.4	17.4
$SCMe_3$	-1.1	35.4
SCH_3	0.3	34.5
SH	0.0	31.7
SF	-0.6	27.1
SCF_3	0.4	21.6
SCN	-6.7	19.8
$SeCH_3$	1.2	30.7
SeH	0.4	27.1
SeF	1.0	21.6
$SeCF_3$	2.1	20.8
SeCN	-1.3	17.9

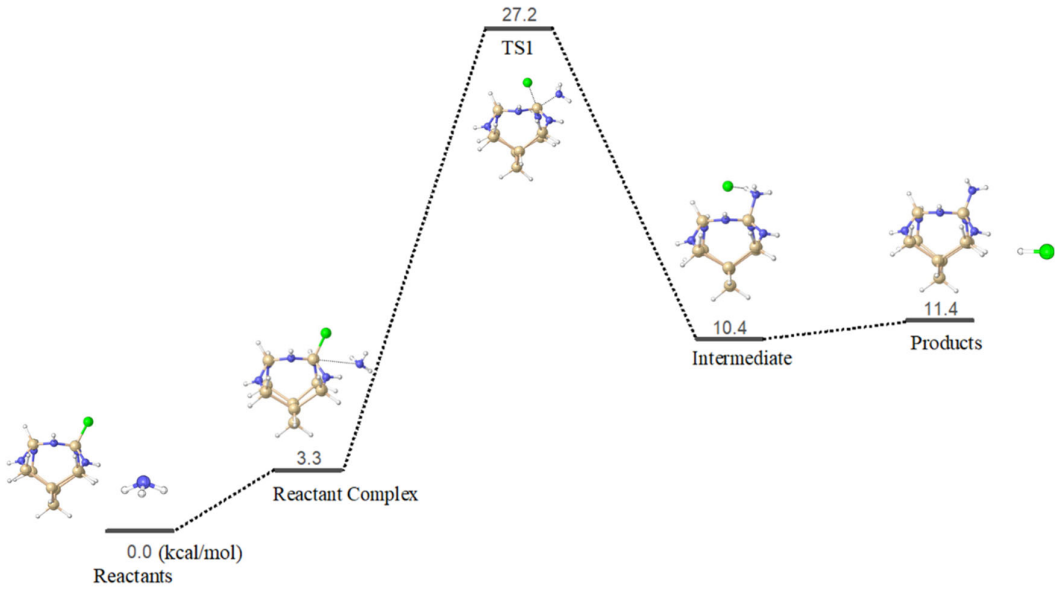


Figure S1: The reaction barrier profile of ammonolysis reaction for X = Cl using cluster model 2 M062X/6-311++G(3df,2p) level. The structures are optimized at M062X/6-311G(d,p) level.